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Abstract

The production of the fire suppressant CF_3Br has been banned, and finding a replacement with all of its desirable properties is proving difficult. Iron pentacarbonyl has been found to be up to several orders of magnitude more effective than CF_3Br , but it is flammable and highly toxic. Ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$), which is much less toxic and flammable than $\text{Fe}(\text{CO})_5$, can also be used to introduce iron into a flame. We present the first experimental data and numerical modeling for the flame inhibition properties of ferrocene, and find it to behave similarly to $\text{Fe}(\text{CO})_5$. A ferrocene mole fraction of 200 ppm reduces the burning velocity of slightly preheated premixed methane-air flames by a factor of two, and the effectiveness drops off sharply at higher mole fractions. The burning velocity reduction is less with an increase in the oxygen content of the air. We also present experimental data and modeling for flames with ferrocene blended with CO_2 or CF_3H . The combination of the thermally acting agent CO_2 with ferrocene mitigates the loss of effectiveness experienced by ferrocene alone at higher mole fractions. An agent consisting of 1.5% ferrocene in 98.5% CO_2 performs as effectively as CF_3Br in achieving a 50% reduction in burning velocity. Likewise, four times less CO_2 is required to achieve the 50% reduction if 0.35% ferrocene is added to the CO_2 . In contrast, addition of 0.35% ferrocene to the hydrofluorocarbon CF_3H only reduces the CF_3H required to achieve the 50% reduction in burning velocity by only about 25%. Thermodynamic equilibrium calculations predict that the formation of iron-fluoride compounds can reduce the concentrations of the iron-species oxide and hydroxide intermediates which are believed to be responsible for the catalytic radical recombination cycles.

Introduction

The production of CF_3Br has been banned. As a flame inhibitor, iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) is about two orders of magnitude more efficient than CF_3Br [1-3], but it is flammable and highly toxic, and its addition to premixed flames at mole fractions above a few hundred ppm* does not further reduce the burning velocity. If other iron compounds can be identified which show the same strong inhibition but are less toxic and do not lose their effectiveness, they may find use in fire suppressants, particularly in

unoccupied areas. Previous research has shown that the moiety responsible for iron pentacarbonyl's strong inhibition is the iron atom in the gas phase, and that the main property required for the parent molecule is that it decomposes at flame temperatures to release iron atom. With this in mind, we search for a suitable iron-precursor molecule. A candidate parent molecule is ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$ or Fec) which modifies the sooting tendency of flames [4-9], is added to materials as a flame retardant [10] and is an antiknock agent. It is also commonly used as a source of iron atoms for kinetic studies. Ferrocene is far less toxic than $\text{Fe}(\text{CO})_5$, and may produce the same iron-containing intermediates. Here, we present the first measurements of flame inhibition by ferrocene, and present results of numerical calculations using the iron-species mechanism developed for studies of $\text{Fe}(\text{CO})_5$ flame inhibition. We also compare ferrocene's performance with that of $\text{Fe}(\text{CO})_5$ and CF_3Br in the same flames, and present results on the performance of Fec in combination with other agents.

Flame inhibition by highly effective chemical inhibitors has been described in the literature, and their reduced effectiveness at higher mole fractions has been discussed in detail [11-13]. Since the chemicals are believed to act through homogeneous gas-phase catalytic radical recombination cycles [14], the inhibition mechanism is most effective when superequilibrium concentrations of radicals are present. Consequently, once radicals are reduced to equilibrium levels via inhibitor addition, further reduction in the overall reaction rate from further inhibitor addition is minimal. This loss in effectiveness due to superequilibrium radical concentrations approaching their equilibrium values has been demonstrated for increasing mole fraction of inhibitor in calculations employing both an idealized "perfect" inhibitor [12] and $\text{Fe}(\text{CO})_5$ [13], and has been discussed by Rosser et al. [15] and Hastie [16]. Nonetheless, the measured loss in effectiveness of $\text{Fe}(\text{CO})_5$ occurs at a lower mole fraction than expected based on these calculations; the actual cause appears to be condensation of iron compounds and the resulting limit to the gas-phase iron-species concentrations [17,18]. Independent of the actual cause of the loss of effectiveness, previous researchers [15,16,19-22] have suggested that combinations of thermally acting

*Note that all references to percent and ppm in the present work are on a volume basis.

and catalytic agents might prove beneficial. The effectiveness of iron pentacarbonyl in premixed flames has been shown to be greatly increased at lower oxygen mole fraction, and the effect has been attributed to the larger superequilibrium ratio (the peak radical mole fraction divided by the equilibrium value) which exists at lower oxygen mole fraction [11]. In contrast, the effectiveness of relatively inert agents such as N_2 and CO_2 is not a strong function of the oxygen mole fraction in the oxidizer stream. Since adding a thermal agent is equivalent to lowering the oxygen mole fraction, the possibility exists for very effective blends of catalytically and thermally acting agents.

The present results are relevant to the suppression of practical fires. Despite the fact that methane oxidation is, in some respects, atypical of that of larger hydrocarbons, the behavior of Fec and $Fe(CO)_5$ in the methane flames is likely to represent that in flames of larger hydrocarbons. Babushok and Tsang [23] have recently observed that for a wide variety of hydrocarbons, the burning velocity is most sensitive to the rates of the same reactions. Since these reactions are the ones most influenced by an inhibitor, the trends in inhibitor effectiveness are the same for most hydrocarbons. Further, although premixed flame inhibition is distinct from fire suppression, premixed flame burning velocity reduction is clearly an important first test of an inhibitor's effectiveness, as has been discussed previously [22]. Nonetheless, it would be desirable in future research to test these highly-effective agents in flames more closely resembling fires.

Experiment

The premixed laminar flame speed S_L provides a measure of the effect of the inhibitor on the overall reaction rate. The present experimental arrangement, described in detail previously [11,22,24], has been modified to accommodate a new evaporator for ferrocene and heating of the gas lines and burner tube. A Mache-Hebra nozzle burner ($1.0\text{ cm} \pm 0.05\text{ cm}$ diameter) produces a premixed Bunsen-type flame about

1.3 cm tall with a straight sided schlieren image that is captured by a video frame-grabber board in a PC. Digital mass flow controllers hold the oxygen mole fraction in the oxidizer stream $X_{O_2,ox}$, the equivalence ratio ϕ , and the flame height constant while maintaining the inlet mole fraction of the inhibitor (X_{in}) at the desired value. The average burning velocity is determined from the reactant flows and the schlieren image using the total area method. The fuel gas is methane (Matheson[†] UHP, 99.9%), and the oxidizer stream consists of nitrogen (boil-off from liquid N₂) and oxygen (MG Industries, H₂O < 50 ppm, and total hydrocarbons < 5 ppm). The inhibitors used are Fec (Aldrich), Fe(CO)₅ (Aldrich), CF₃H (DuPont), CF₃Br (Great Lakes), N₂, and CO₂ (Airgas). The Fe(CO)₅ is added to N₂ carrier gas using a two-stage saturator in an ice bath. Because the vapor pressure of Fec is much lower than that of iron pentacarbonyl, Fec addition at mole fractions up to 650 ppm requires both higher bath temperature (79.1 °C held within 0.1 °C) and higher nitrogen carrier gas flow rates (up to 2800 cm³/min) relative to Fe(CO)₅. Also, the solid state of Fec requires an evaporator with larger surface areas for heat and mass transfer. Our evaporator design, based upon that of Megaridis [5], has a (30 ± 5) cm³ packed bed (to provide the bulk of the ferrocene), followed by thirty sublimation stages (to insure that the carrier gas is saturated with Fec at the bath temperature). Each sublimation stage consists of a 5 mm layer of ferrocene on a 2.36 cm diameter 60 mesh stainless steel screen. A 4 mm gap separates each stage. The vapor pressure correlation of Pelino et al. [25] is used to determine the ferrocene mole fraction in the carrier gas. Temperature controllers maintain the transfer lines at (80 ± 3) °C and the burner tube at (80 ± 1) °C. For all flames, the equivalence ratio (in the absence of inhibitor) is 1.0, and agent mole fraction is calculated relative to the total reactant flow. The flows of fuel, oxidizer, Fec-N₂, and CO₂ (or CF₃H) are mixed after the Fec evaporator. The inlet reactant stream temperature is (353 ± 1), K which corresponds to a calculated adiabatic flame temperature of 2260 K and 2391 K at $X_{O_2,ox} = 0.21$ and 0.244 respectively. Addition of 200 ppm of Fec raises the calculated adiabatic flame temperature by only a few degrees.

[†] Certain commercial equipment, instruments, or materials are identified in this paper to adequately specify the procedure. Such identification does not imply recommendation or endorsement by the National Institute of

Numerical modeling

One-dimensional freely-propagating premixed flames are simulated using the Sandia flame code *Premix* [26], the *Chemkin* subroutines [27], and the transport property subroutines [28]. For all of the calculations the absolute tolerance is 10^{-14} , the relative tolerance is 10^{-9} , GRAD is 0.20, and CURV is 0.40. Solutions typically contain between 85 and 130 grid points. The initial temperature is 353 K and the pressure is one atmosphere. Little is known about the chemical kinetic behavior of ferrocene in flames. The thermal decomposition rate has been measured by Lewis and Smith [29]: $k = 2.188 \cdot 10^{16} \exp(-384 \text{ kJ/RT})$. However, the high activation energy suggests the ferrocene could be consumed through reactions with radicals and this possibility should be investigated further. Thermodynamic data for gaseous ferrocene are from Turnbull [30] and Sabbah and Perez [31], and the transport properties are estimated [32,33]. A reaction set for the methane combustion and for the decomposition and oxidation of the larger hydrocarbon fragments was adopted from Sung et al. [34]. The mechanism includes chemistry of C6 compounds, with C1 and C2 chemistry from GRI-Mech 1.2 [35], and with C3 and above chemistry from a variety of sources. We added iron chemistry from a chemical kinetic mechanism developed for flame inhibition by $\text{Fe}(\text{CO})_5$ [36]. Overall, the kinetic model contains 105 species and 677 reactions. Calculations showed that addition of C_5H_5 at mole fractions up to 400 ppm had negligible effect on the burning velocity, and that the major effect of Fec is from the iron chemistry. Consequently, we also employ a reduced mechanism based on GRI-Mech 1.2 and the iron-inhibition mechanism described in ref. [36]. In this smaller mechanism, the decomposition of Fec is approximated by a one-step process with an overall activation energy of 209 kJ/mol, followed by a reduced scheme for conversion of C_5H_5 to simpler hydrocarbons. This lower activation energy is selected to more realistically simulate the overall decomposition rate of Fec. In the calculated results for the Fec-inhibited flames presented in this paper, the two mechanisms yield normalized burning velocities within a few percent of each other; in the figures

which follow, the calculated burning velocities are obtained using the smaller mechanism. It should be emphasized that the reaction mechanism used for the present calculations should be considered only as a starting point. Numerous changes to both the rates and the reactions incorporated may be made once a variety of experimental and theoretical data are available for testing the mechanism.

Results and Discussion

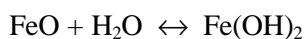
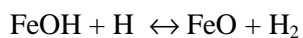
Inhibition by Ferrocene

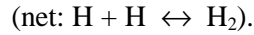
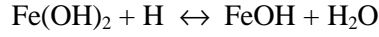
The experimentally determined burning velocity reduction caused by the addition of Fec or $\text{Fe}(\text{CO})_5$ to stoichiometric methane flames is presented in Figure 1. (The uncertainties in the experimental data, described in detail previously [37], are typically about $\pm 5\%$.) As the figure shows, addition of Fec (open symbols) is similar to the addition of iron pentacarbonyl (closed symbols). Data are plotted as normalized burning velocity, which is the burning velocity of the inhibited flame divided by the value for the same flame in the absence of inhibitor. The uninhibited experimental burning velocities used for the normalizations are (53.7 ± 3) cm/s and (75.9 ± 6) cm/s for $X_{\text{O}_2, \text{ox}} = 0.21$ and 0.244 respectively; for comparison, the calculations for uninhibited flames using GRI-Mech 1.2 yield 55.5 cm/s and 72.6 cm/s. Data collected at slightly fuel lean and fuel rich conditions ($\phi = 0.9$ and 1.1), but not presented here, show that the slope of the burning velocity reduction is about twice as steep for the lean conditions compared to the rich conditions, and that the Fec loses its effectiveness at a somewhat lower mole fraction for the lean case (again, essentially the same as was observed for $\text{Fe}(\text{CO})_5$ -inhibited methane flames in Ref. [11]). Figure 1 shows that for both Fec and $\text{Fe}(\text{CO})_5$, the magnitude of the inhibition is strongly dependent upon the oxygen mole fraction in the oxidizer, with oxygen-deprived flames showing more rapid burning

velocity reduction. These results foretell the potential of blends of inert agents with iron-containing compounds.

The modeling results for the ferrocene-inhibited flames are also shown in the figure. The calculations (dotted lines) predict the flame speed reduction caused by ferrocene reasonably well. The major difference between the ferrocene reaction scheme and that for $\text{Fe}(\text{CO})_5$ is in the decomposition of the iron precursor. The present large mechanism for ferrocene includes only the high-activation energy thermal decomposition step for Fec consumption $\text{FeC}_{10}\text{H}_{10} \rightarrow \text{Fe} + 2 \text{C}_5\text{H}_5$, which has a peak reaction flux at 1800 K in the present flames. In contrast, iron pentacarbonyl decomposition has a peak reaction flux at about 900 K. Figure 2 shows the normalized burning velocity for a methane-air flame with 400 ppm of ferrocene as a function of the activation energy E_a of the one-step decomposition reaction. In the temperature range of the stoichiometric methane-air flame of the figure, the predicted inhibition effect of Fec is independent of the overall activation energy of the decomposition of Fec for values of E_a less than about 350 kJ/mol. Hence, the decomposition rate of Fec used in the model does not influence the predicted behavior. For other conditions, however, (for example non-preheated reactants and highly diluted flames) the decomposition of Fec may need to be modeled more accurately to provide agreement with experimental data.

Since both the Fec and $\text{Fe}(\text{CO})_5$ mechanisms use the same iron sub-mechanism, the mode of flame speed reduction is the similar. Decomposition of the ferrocene molecule releases iron atom in the gas phase. Iron reacts with O_2 to form FeO_2 , which reacts with O atom to form FeO . FeO is a long-lived intermediate, which together with $\text{Fe}(\text{OH})_2$ and FeOH , enters into the catalytic cycle for H-atom recombination





The modeling results show that the stronger burning velocity reduction for the cooler flames ($X_{O_2,ox} = 0.21$) is due to their smaller radical pool; in these flames, a given amount of iron can remove a larger *percentage* of the hydrogen radicals.

Ferrocene appears to be an alternative to the highly toxic iron pentacarbonyl for addition of gas-phase iron to a flame. Unfortunately, its effectiveness also appears to diminish as the mole fraction increases. (For Fe(CO)_5 the loss of effectiveness has been identified to be formation of condensed-phase particulates in the reaction zone[18]). Since addition of nitrogen clearly increases the rate of burning velocity reduction at low mole fraction (note the results in Figure 1 for $X_{O_2,ox} = 0.21$ and 0.244), it is of interest to determine if other thermally acting agents can be combined with Fec to mitigate the loss of effectiveness, and perhaps enhance the flame speed reduction at low Fec mole fraction. It is desired to take advantage of the strong initial flame speed reduction from iron species in the flame, while avoiding the loss of active species due to condensation. A drawback, however, is that addition of an inert, while reducing the burning velocity, also increases the residence time for particle formation in the flame, so that condensation is increased [18]. It is not known a priori if the net effect of combining thermal and iron-containing agents will reduce the overall reaction rate faster than the increase of the rate of active-species condensation.

Inhibition by Ferrocene Blends

Figure 3 presents experimental data for addition of pure CO_2 (and pure N_2) as well as for CO_2 -Fec blends corresponding to five values of the percentage of Fec in CO_2 : 0, 0.05%, 0.25%, 0.53 and 1.5%. For the pure compounds, addition of about 10% of CO_2 (or 25% N_2) reduces S_L by a factor of two. Although not presented in the figure, tests at $X_{O_2,ox} = 0.244$ also show that about 10% CO_2 is required to reduce the

burning velocity by a factor of two. Adding Fec to CO₂ produces a particularly effective agent. The equivalent of 0.25% Fec in CO₂ reduces the required CO₂ by about a factor of three, and 1.5% Fec reduces the required CO₂ by ten, making this blend about as effective as CF₃Br (for which addition of about 1% halves the burning velocity). Nonetheless, it does appear that blends with higher Fec/CO₂ ratios experience some loss of effectiveness as their mole fraction increases, likely due to iron-species condensation. Although one might expect the slightly cooler, slower flames with added CO₂ to always show more condensation of iron species, the greater efficiency of the catalytic cycle in the diluted flames predominates for most of the conditions for the flame of Figure 3.

The condensation behavior of the blends can be discerned from Figure 4, which presents additional data for CO₂ and ferrocene in stoichiometric flames with $X_{O_2,ox} = 0.21$. In Figure 3, the CO₂ and ferrocene were added together in proportional amounts, whereas in Figure 4, CO₂ is first added at a constant mole fraction (0, 1, 2, 3, and 6%), and then the Fec is added. This approach allows a clearer delineation of the effects of each component of the blend. As Figure 4 shows, the curve with 0% CO₂ (pure Fec) has a decreasing slope magnitude as X_{in} increases (due to increased condensation). For each of the other curves, the added amount of CO₂ reduces the normalized burning velocity before the Fec is added, so that each curve starts at a value less than unity; addition of Fec further reduces the flame speed. Below an Fec mole fraction of about 70 ppm, the curves are all roughly parallel, but any curve which extends out beyond this value shows a decreasing effectiveness. For the range of conditions of the figure, the added CO₂ (and consequent lower temperature and higher particle residence time) does not cause a more rapid loss of effectiveness. Rather, higher Fec mole fractions appear to be related to the loss in effectiveness. These results imply that combinations of *non-condensing quantities* of several catalytic agents combined with a thermal agent can be particularly effective.

Many compounds are candidates for blending with catalytic agents, including thermally acting and other chemical agents. Hydrofluorocarbons, which are easily stored at relatively low pressure, are of interest since they are presently used as halon replacements. These compounds have been found to reduce the burning velocity of premixed methane-air flames by reducing *peak* H-atom mole fractions by acting as a sink for H atoms through reactions forming HF, and by lowering the temperature of the flame. Since they have also been shown to reduce the *equilibrium* mole fractions of radicals in flames lower than expected based on temperature reduction alone [38], they might be expected to show enhanced performance relative to CO₂ when combined with catalytic agents.

Figure 5 presents the burning velocity reduction caused by pure CF₃H addition to the above flames; a mole fraction of about 5% is required to reduce S_L by two. Data are also presented for addition of 0.35% Fec in CF₃H. Unlike ferrocene addition to CO₂, in which 0.35% Fec in CO₂ reduces the amount of CO₂ required by a factor of about five, this amount of ferrocene in CF₃H reduces the amount of CF₃H required only by about a third. This poor performance may be due to reactions between iron species and fluorine which reduce the gas-phase mole fraction of the active iron-species intermediates, effectively poisoning the iron catalyst [16].

Since there presently exist no experimental data on the rates of reactions of iron species with fluorine containing species in flames, the poisoning effect of fluorinated hydrocarbons on iron-catalyzed radical recombination reactions is assessed through equilibrium calculations for the combustion products. The species included in the calculations are those in the hydrocarbon, the iron-inhibition, and the NIST C1-C2 fluorinated hydrocarbon [39] mechanisms, as well as the iron-fluorine species: FeF, FeF₂, FeF₃, Fe₂F₄, Fe₂F₆ [40]. Calculations were performed for the equilibrium products of a stoichiometric methane-air flame with 1 to 4% CF₃H containing 0.35% Fec (the conditions of Figure 5). The results are presented in Figure 6, which shows the equilibrium mole fractions of FeF, FeF₂, and FeF₃ together with those of the active inhibiting iron species Fe, FeO, FeOH, FeO₂, and Fe(OH)₂, as a function of the CF₃H mole percent.

The figure indicates the presence of relatively large quantities of fluorinated iron species (especially FeF_2), which increase in proportion as $[\text{CF}_3\text{H}]$ increases. The formation of fluorinated iron species with strong bonds can clearly act as a sink for iron in the flame, and reduce the mole fractions of active iron-containing species available to participate in the flame inhibition reactions. While the experiments and calculations are presented for CF_3H , the results are likely to be similar for larger HFCs such as C_2HF_5 and C_3HF_7 since the decomposition of each proceeds largely through the CF_3 , CF_2 , and CFO intermediates [24,38,41].

Conclusions

We have presented the first data on ferrocene as a flame inhibitor, and shown it to be as efficient as $\text{Fe}(\text{CO})_5$ at reducing the burning velocity of premixed methane flames. Ferrocene, like $\text{Fe}(\text{CO})_5$, loses its effectiveness at a mole fraction above a few hundred ppm. The experimental results are reasonably predicted by a previously developed mechanism for gas-phase inhibition by iron pentacarbonyl. The results imply that any rapidly decomposing iron-containing agent that releases atomic iron in the gas phase can act as an effective precursor for the active iron-species intermediates, and that the results are not unique to $\text{Fe}(\text{CO})_5$. As with iron pentacarbonyl, the magnitude of the inhibition by ferrocene has a strong dependence on the oxygen mole fraction. As a result, many combinations of CO_2 and Fec show strong inhibition, mitigating the loss of effectiveness observed for pure Fec or $\text{Fe}(\text{CO})_5$. The results imply that an inert agent, together with multiple catalytic agents (to keep the absolute mole fraction of each below the saturation point) may prove to be highly effective for all conditions. In contrast to the results with CO_2 , blends of CF_3H and Fec are not particularly effective, implying that iron species and halogens may enter into undesired reactions which poison the catalytic cycles. If means can be identified to safely introduce gas-phase iron compounds into fires, combinations of catalytically and relatively inert thermally acting inhibitors may prove to be an efficient approach for developing effective fire suppressants. Additionally, since gas-phase iron from ferrocene can greatly affect radical mole fractions in flames, it

may be of interest for soot researchers to examine if changes in the radical pool from iron reactions are affecting the soot formation or burnout for flames with added ferrocene, a known soot suppressant.

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List of Figures

Figure 1 – Normalized burning velocity of premixed $\text{CH}_4/\text{O}_2/\text{N}_2$ inhibited by ferrocene (open symbols) and $\text{Fe}(\text{CO})_5$ (closed symbols) for values of $X_{\text{O}_2, \text{ox}} = 0.21$ and 0.244 , together with numerical modeling predictions (dotted lines).

Figure 2 – The normalized burning velocity of stoichiometric $\text{CH}_4/\text{O}_2/\text{N}_2$ flames at 400 ppm of Fec as a function of the activation energy of the one-step ferrocene decomposition reaction.

Figure 3 - Normalized burning velocity of $\text{CH}_4/\text{O}_2/\text{N}_2$ flames inhibited by CO_2 , by CO_2 –ferrocene blends, and by CF_3Br . The equivalent percentage of ferrocene in CO_2 (which is constant for each curve) is given. The solid lines are curve fits through the data, and the dotted lines, the calculated results.

Figure 4 – Normalized burning velocity of $\text{CH}_4 / \text{N}_2 / \text{O}_2$ flames with 0, 1, 2, 3, and 6 mole percent of CO_2 added to the reactant stream, as a function of added ferrocene (lines are curve fits to the experimental data).

Figure 5 – Normalized burning velocity of premixed $\text{CH}_4/\text{O}_2/\text{N}_2$ flames inhibited by pure CF_3H and by CF_3H with 0.35% ferrocene, together with data for CF_3Br . Lines are curve fits to the data.

Figure 6 – Equilibrium mole fraction of active inhibiting species (Fe , FeO , FeOH , $\text{Fe}(\text{OH})_2$) and iron-fluorine species with 1% to 4% CF_3H (containing 0.35% ferrocene) added to a stoichiometric methane-air reaction mixture.

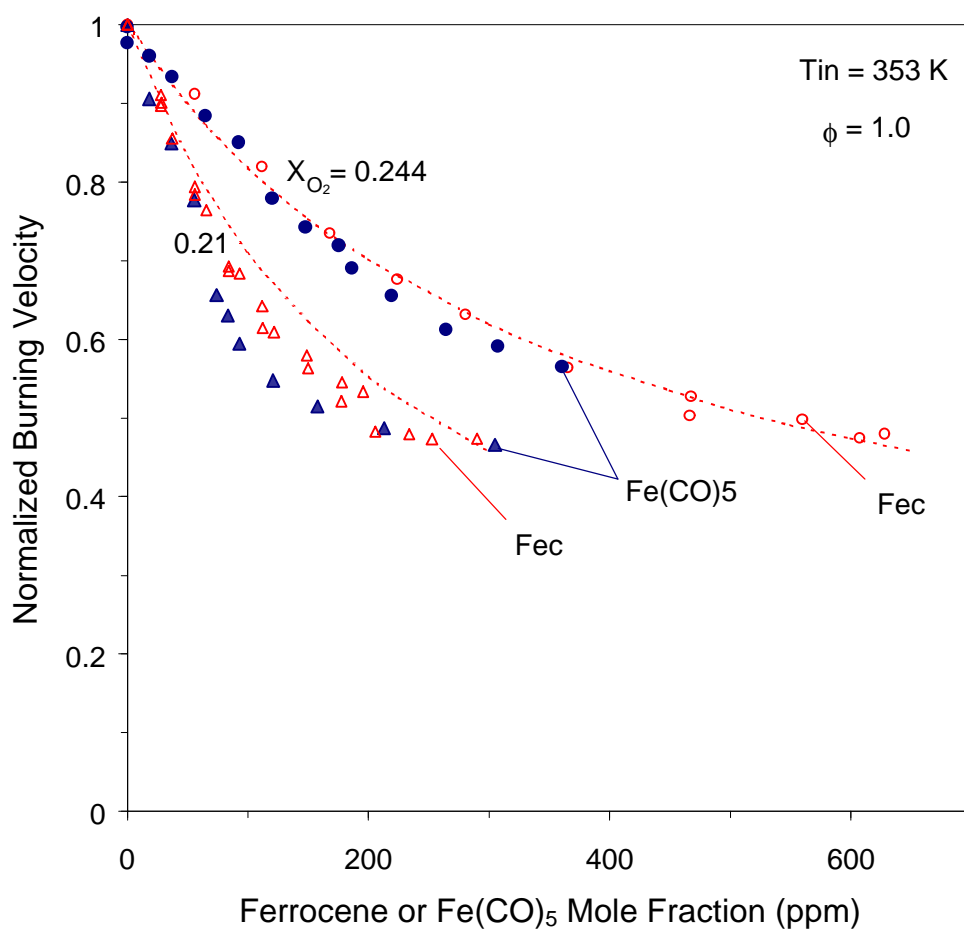


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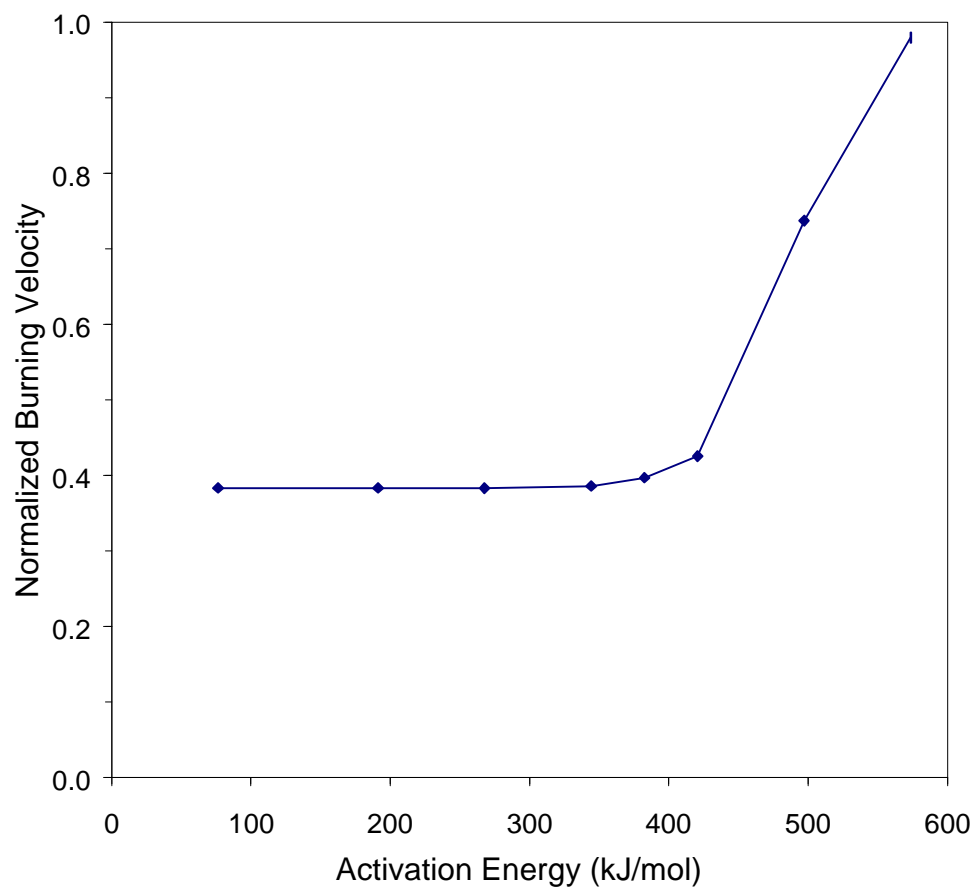


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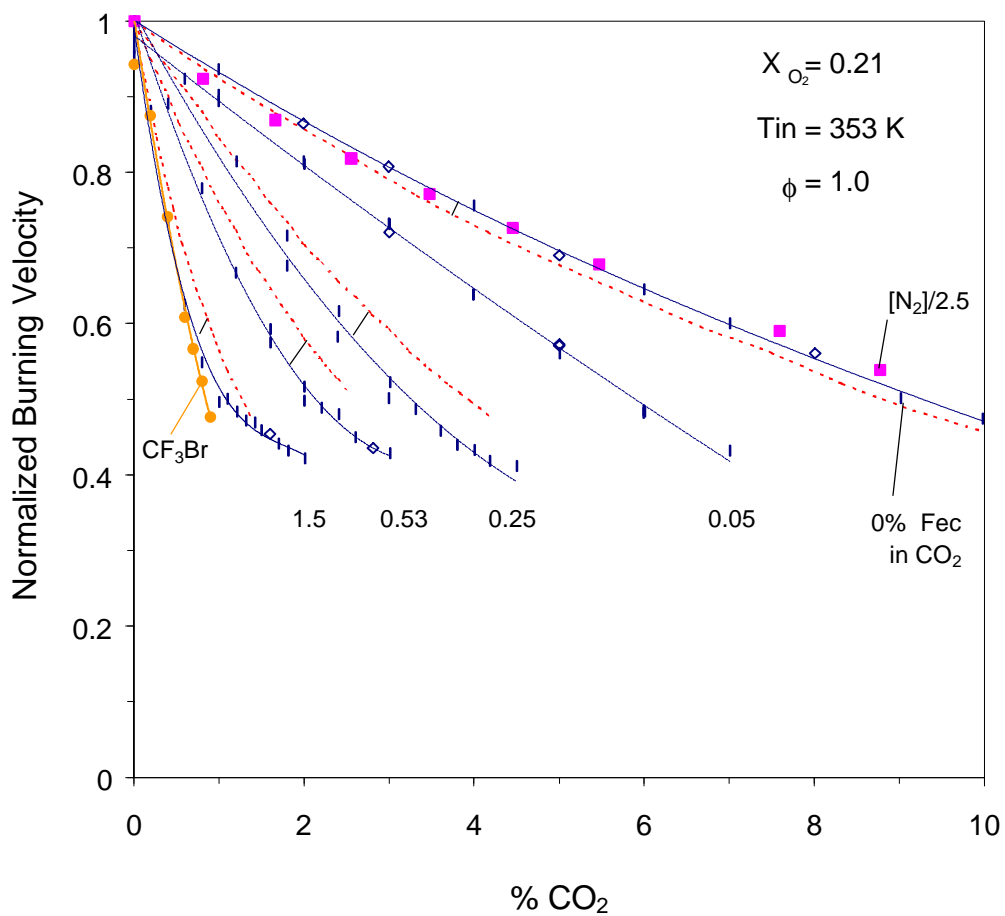


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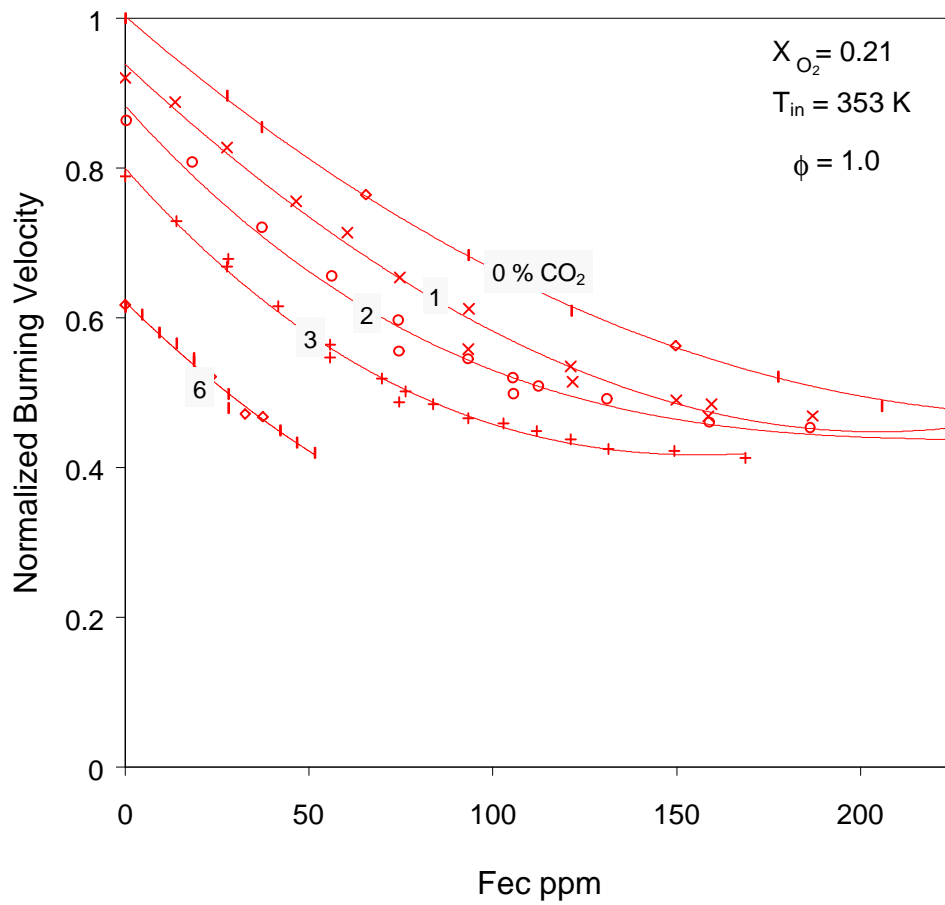


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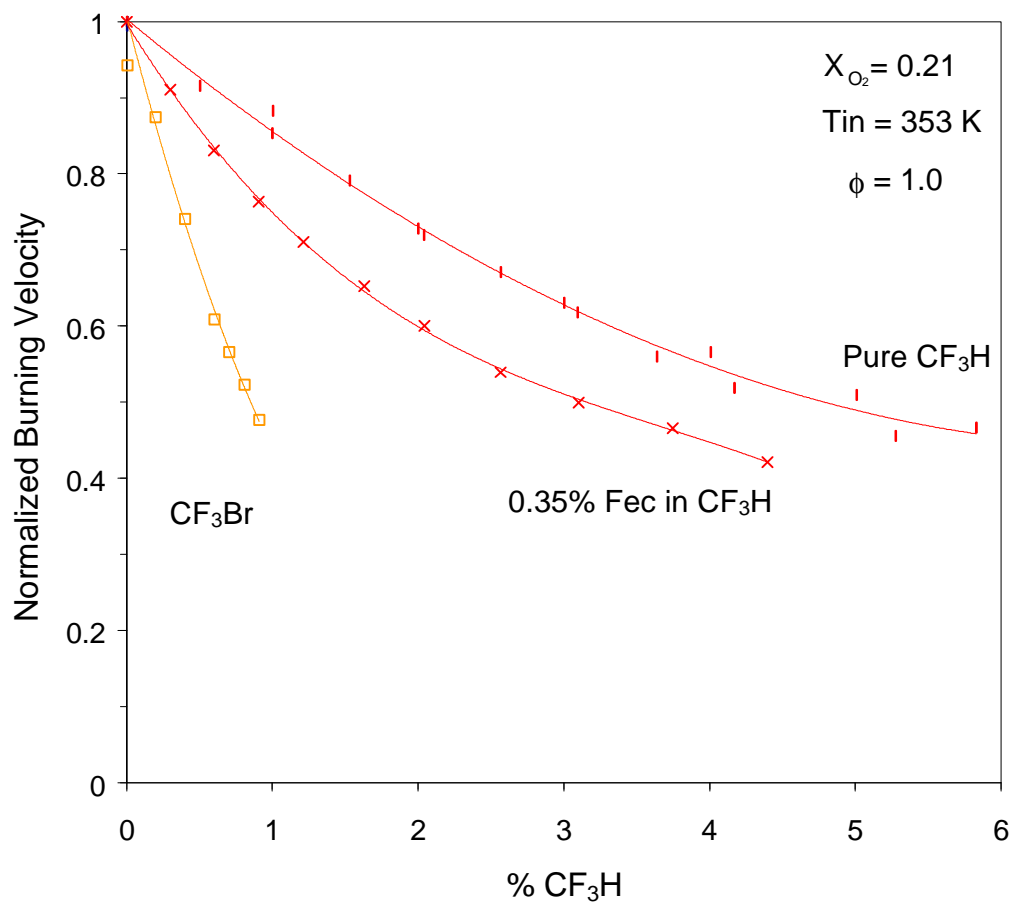


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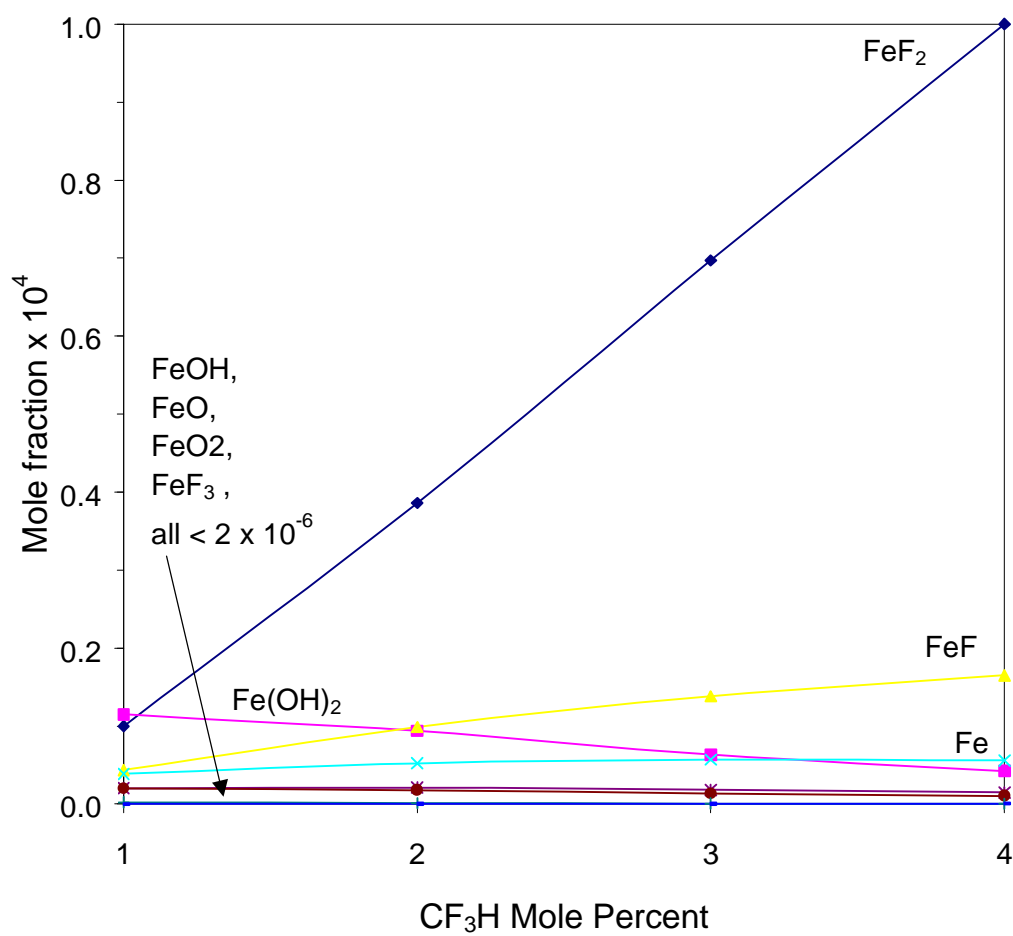


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